Renewable and Sustainable Energy Reviews 15 (2011) 4432–4435

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Bioethanol production from farming non-food macroalgae in Pacific island nations: Chemical constituents, bioethanol yields, and prospective species in the Philippines

M.G. Borines[a,*], R.L. de Leon[b], M.P. McHenry[c]

[a] College of Engineering and Agro-industrial Technology, University of the Philippines, Los Baños, College, 4031 Laguna, Philippines
[b] College of Engineering, University of the Philippines, Diliman, Quezon City, Philippines
[c] School of Energy and Engineering, Murdoch University, Western Australia, Australia

ARTICLE INFO

Article history:
Received 22 March 2011
Accepted 5 July 2011
Available online 15 September 2011

Keywords:
Renewable biofuel
Bioethanol
Mariculture
Macroalgae
Sargassum spp.

ABSTRACT

Increasing biofuel production on agricultural lands in tropical island nations will likely result in increased deforestation [1], and also inflate food prices, especially in net food importing countries like the Philippines [2–4]. Compounding problems associated with promotion of biofuels in southeast Asian countries are the technical efficiencies of bioethanol production, including poor energy balances from terrestrial crops that are close to, or less than unity, unless bagasse is used as the distillation heat source [1]. As the increase in terrestrial biofuel production in Pacific island nations is potentially less sustainable than is publically stated, alternative feedstocks are required which retain the regional development benefits, while reducing the negative ecological and food security impacts [1,5]. This work presents the potential of farmed macroalgae chemical substrates as a bioethanol feedstock supply, explores macroalgae-to-bioethanol yields, and details prospective non-food macroalgae species, specific to the Philippine coastal region. Leveraging off the existing capability of the macroalgae farming industry (producing 1.7 million wet tonnes annually in the Philippines alone), a significant new market for non-food macroalgae stimulated by bioethanol producers can be developed to avoid problems related to food/feed grade ethanol feedstocks.

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Contents

1. Introduction

1.1. The current status of bioethanol demand and production in the Philippines

According to the Philippine's Department of Energy (DOE), the Philippines required around 219 mL of bioethanol in 2010 to comply with the 5% by volume gasoline blending mandate, as per the Biofuel Act of 2006 (RA 9367). The Act's blending rate increased to 10% (by volume) in 2011, which is expected to displace around 461 mL of mineral fuel demand (Table 1). By 2014, the general increase in national fuel consumption is projected to increase bioethanol demand to 536 mL annually [6]. National deforestation and food security risks from the increasing biofuel demand requires judicial industrial development [1–5]. As of 2009, there were only two local bioethanol producers, Leyte Agri Corp, and San Carlos Bioenergy Inc. The Leyte Agri Corp commenced bioethanol

* Corresponding author. Tel.: +63 049 536 2315.
E-mail address: mgborines@yahoo.com (M.G. Borines).

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doi:10.1016/j.rser.2011.07.109

Table 1
Projected bioethanol demand, based on projected gasoline consumption in the Philippines.

Year	Gasoline demand (mL)	Bioethanol blend required by the Biofuels Act 2006	Fuel displacement (mL)
2006	3,574.96	–	–
2007	3,760.86	–	–
2008	3,956.43	–	–
2009	4,162.16	5%	208.11
2010	4,378.59	5%	218.93
2011	4,606.28	10%	460.63
2014	5,362.87	10%	536.29

Source: [6].

production in late 2008, with an approximate annual production capacity of 9 mL. The San Carlos Bioenergy Inc., the larger facility of the two, commenced operation in late 2009 as an integrated sugar mill, cogeneration plant, and distillery, with an estimated annual bioethanol capacity of 30 mL [7]. In 2011, the Ethanol Producers Association of the Philippines reported that approximately 80 mL will be produced [8]. However, these production figures translate to annual domestic production deficit of 170 mL in 2009 and 140 mL in 2011. Currently, the shortage of domestic bioethanol is met by importing bioethanol from Brazil [7,9]. To redress the domestic deficit, the Philippine Government plans to develop a USD5 million, 100 ha bioethanol macroalgae farm in the province of Aurora in Luzon, using technology developed by the Korean Institute for Industrial Technology [10].

2. Macroalgal biomass as a bioethanol feedstock

Macroalgae are a promising bioethanol feedstock due to their fast growth rate and large biomass yield, with superior productivity to many terrestrial crops [11]. (Table 3 compares macroalgae with conventional terrestrial bioethanol feedstocks, such as sugarcane, corn, and wheat). The high yield of macroalgae is attributed to their lower energy requirement for the production of supporting tissues than terrestrial plants, in addition to their capability to absorb nutrients over their entire surface area [11], and the energy-savings derived from zero requirements for internal nutrient transport [12]. Many types of seaweed exhibit a mass productivity of 13.1 kg dry weight m^{-2} over a seven month growth period, compared to terrestrial plants achieving 0.5–4.4 kg dry weight m^{-2} over an entire year [12–14]. Furthermore, macroalgae generally have a greater hydrolysable carbohydrate content, and potential volume of ethanol than current bioethanol feedstocks [11].

Table 2
Chemical composition of *Ascophyllum nodosum*.

Component	%	Comments
Water	67–82	Decreased with salinity and lowered during the spring
Ash	18–24	Increased from autumn to spring
Alginic acid	24–29	Fluctuates during the year
Laminarin	1.2–6.6	Increased from spring to late autumn
Mannitol	6.8–10.4	Increased from early spring to early autumn
Fucoidan	4–10	
Other carbohydrates	10	
Protein	4.8–9.8	Increased from autumn to spring
Fat	1.9–4.8	Increased from early spring to late autumn
Fibre (cellulose)	3.5–4.6	Almost constant throughout the year
Polyphenols	0.5–14	Lower during spring and increased greatly with salinity

Source: [35].

2.1. Chemical characteristics of macroalgae

Macroalgae are historically divided into three major groups based on their photosynthetic pigments: Chlorophyta (green algae), Rhodophyta (red algae), and Phaeophyta (brown algae) [16,17]. The majority of the pigments in green algae are chlorophylls a and b. The photosynthetic product of green macroalgae is starch, and the outer and inner layers of their cell wall are predominantly pectin and cellulose, respectively [18]. The red macroalgae pigment is r-phycoerythrin, and the cell walls contain small amounts of cellulose, while the majority is gelatinous or amorphous sulfated galactan polymers, such as agar, carageenan, funoran, etc. Brown macroalgae colouration is due to the predominance of xanthophyll pigments, especially fucoxanthin [16]. Brown macroalgae cell walls are composed of alginic acid, cellulose, and other polysaccharides. The food reserves of this group are the carbohydrates laminarin and mannitol, which are particularly suited to ethanol production [19,20].

Macroalgae with high carbohydrate contents are promising candidates for bioethanol production, including: *Sargassum, Gracilaria, Prymnesium parvum*, *Euglena gracilis*, *Gelidium amansii* [12], and *Laminaria* [15]. Macroalgae carbohydrate contents vary widely by species and cultivar, and species selection can develop strains with very high contents of carbohydrate for use as an efficient bioethanol feedstock. Brown macroalgae such as *Laminaria* spp. contain up to 55% (dry weight) of carbohydrates laminarin and mannitol [15,21]. This work focuses on the suitability of the *Sargassum* spp., a brown macroalgae which has relatively high carbohydrate content. (Table 4 shows the results of proximate analyses of two species of Philippine *Sargassum* macroalgae).

The brown macroalgae carbohydrates consist of primarily cellulose, hemicellulose, free sugars, and also the energy storage molecules laminarin and mannitol [19]. As crude fibre is composed of cellulose and hemicelluloses, the % carbohydrates in Table 4 only constitute the storage products and free sugars. However, macroalgae constituents are not constant throughout the year. As an example, research by Horn [21] on the composition of brown algae, *Ascophyllum nodosum* (Table 2), describes seasonal component flux, and also includes indicative magnitudes for each component during the year. The brown algae described in Table 2 are comprised of around 24–29% alginic acid, a polymer of D-mannuronic and L-guluronic acids covalently linked together in sequence. Alginic acid is a common polysaccharide found in the cell walls of brown algae, and in extracted form it quickly absorbs water, making it useful as an additive in dehydrated products, paper and textile manufacture, in addition to use as a food thickener and stabiliser [16]. On a dry weight basis, the amount of alginic acid in brown seaweed is usually between 10% and 25%, which is dependent somewhat on the depth of the seaweed grown in the farm [21]. Therefore, the location, time of year, and the unique habitat all influence alginic acid production, which needs to incorporated in farming design and planning [22].

Laminarin is a storage glucan (a polysaccharide of glucose) found in brown algae and is used as a carbohydrate food reserve. It is a linear polysaccharide made up of β (1,3)-glucan [25]. Mannitol is a low molecular mass sugar alcohol composed of carbon, hydrogen, and multiple hydroxyl groups. In addition to mannitol forming a component of the laminarin molecule, mannitol performs an osmoregulatory role in macroalgae [26]. Glucanases are relatively common, and many microorganisms can hydrolyse laminarin to its glucose monomer, a suitable fermentation substrate. However, mannitol is not readily fermented as many microorganisms are not able to perform strictly anaerobic fermentation of mannitol [21]. Therefore, mannitol must be oxidised to fructose by the enzyme mannitol dehydrogenase to produce the reduced from of nicotinamide adenine dinucleotide (NADH) [21,27].

Table 3
Comparisons of yield, hydrolysable carbohydrate, and potential bioethanol production between major terrestrial bioethanol crops and macroalgae.

	Wheat (grain)	Corn (kernel)	Sugar beet	Sugarcane	Macroalgae
Average world yield (kg ha^{-1} $year^{-1}$)	2800	4815	47,070	68,260	730,000
DW of hydrolysable carbohydrates (kg ha^{-1} $year^{-1}$)	1560	3100	8825	11,600	40,150
Potential volume of bioethanol (L ha^{-1} $year^{-1}$)	1010	2010	5150	6756	23,400

Source: [15].

Table 4
Proximate analyses of Philippine *Sargassum* spp.

Species	% Moisture	% Ash	% Crude fibre	% Crude fat	% Crude protein	% Carbohydrates (by difference)
Sargassum kushimonte[a]	12.43	26.67	11.53	0.12	6.37	42.89
Sargassum cristaefolium[b]	13.07	24.90	16.10	0.17	5.09	46.78

Sources: [[a]23, [b]24].

3. Recent macroalgae fermentation techniques and results

Macroalgae are gaining some attention as an alternative renewable source of biomass for the production of bioethanol, although algal fermentation facilities are relatively expensive to construct and operate, although are known to be reliable and produce high yields with a range of feedstocks [28]. Fermentation is usually undertaken using yeasts, although some bacteria can be utilised. Research by Horn et al. [21] demonstrated the possibility of fermenting extracts from *Laminaria hyporbea* (a brown algae) to ethanol using *Pichia angophorea* (a yeast) with a maximum yield of 0.43 g ethanol per g of substrate. Further research by Horn et al. [27] focussed on production of ethanol from synthetic mannitol using the bacterium *Zymobacter palmae* under different oxygen regimes. The bacteria successfully grew and produced bioethanol in the synthetic mannitol medium under oxygen-limiting conditions, with a yield of 0.38 g ethanol per g of mannitol. In the same work, Horn et al. [27] used glucose and mannitol as a mixed substrate in combination with an extract from *L. hyporbea* to determine the efficacy of the bacteria to ferment mannitol from *L. hyporbea* extracts. The ethanol yields were 0.53 g ethanol per g of mannitol after 11.7 h, and 0.61 g ethanol per g of mannitol at 21.9 h. Further research by Adams et al. [15] explored ethanol production using laminarin from *Saccharina latissima* (a brown macroalga) fermented with *Saccharomyces cerevisiae* (a yeast) with a range of pre-treatments. The results indicated that pre-treatments prior to fermentation were not required for the fermentation process, and higher ethanol yields were achieved in untreated fermentation than those with altered pH or temperature pre-treatments, both for fresh and defrosted macroalgae samples. The highest ethanol yield achieved was 0.45% (by volume) [15]. These findings are contrasted with pretreatment research for other groups of macroalgae. Wi et al. [12] investigated fermentation pretreatments for a red macroalgae species exhibiting high carbohydrate contents (typically 23% galactose and 20% glucose) known as Ceylon moss (*G. amansii*). The results found using sodium chlorite prior to enzymatic saccharification, glucose yields of up to 70% were obtained, while only 5% glucose yields were attained without pretreatment. The research also found that efficiency of enzymatic hydrolysis was significantly improved by sodium chlorite pretreatments. This demonstrates the additional potential of pretreatment methods for increasing the scope of macroalga species suitable for farming for bioethanol production. A study by Ge et al. [29] explored the use of macroalgae floating residue wastes from the *Laminaria japonica* (a brown algae) alginate industry for ethanol production and the use of diluted sulphuric acid pretreatments and enzymatic hydrolysis consisting of cellulose and cellobiose. The research found the residues exhibited high cellulose, low hemicelluloses, and low lignin contents, and determined that existing farm residues were a promising feedstock for bioethanol production, and that cellulose in processing wastes including floating residues are successfully hydrolysed to produce glucose [29]. These results suggest that in addition to farming of *Sargassum*, additional species (post treatment) and wastes from existing food-grade production may be suitable input streams to supplement both macroalgae and conventional fermentation feedstocks.

4. *Sargassum* spp. as bioethanol feedstock in Pacific island nations

The genus *Sargassum* is widely distributed in tropical and subtropical seas. It is the most dominant and abundant alginophyte in tropical areas. In the Philippines, the *Sargassum* spp. are the largest among the marine algae [18], and are abundant over rocky, wave exposed, or sheltered areas of the country [30]. The beds of *Sargassum* usually occur near coral reefs where they attach to rocky substrates along reef margins [18]. More than 20 *Sargassum* spp. have been documented in the Philippines [31], the most common include *Sargassum crassifolium*, *Sargassum cristaefolium*, *Sargassum oligosystum*, *Sargassum binderi*, *Sargassum cinctum*, *Sargassum feldmannii*, *Sargassum hemiphyllum*, *Sargassum polycystum*, *Sargassum paniculatum* and *Sargassum siliquosum* [32]. Montaño [33] reported that there are at least 50 distribution sites for *Sargassum* in the Philippines, however, at present there is no commercial production for alginate from *Sargassum* in the Philippines, although pilot studies have been completed [32].

While commercial macroalgae farming is common in the coastal areas of Jolo, Tawi-tawi, Zamboanga del Norte, Zamboanga del Sur, Palawan, Bohol, the Visayas, and Mindanao, *Sargassum* spp. are not currently in production. According to Trono [32], the current harvesting of local stocks of *Sargassum* is minor and limited to certain areas in Northern Mindanao and Visayas. Currently, the most common use of *Sargassum* spp. in the Philippines is as a wrap to maintain the freshness of fishery catches, while minor amounts are used as a feed for pigs and cattle in coastal areas, or dried for export as animal feed [30,32]. Therefore, as *Sargassum* spp. markets are underdeveloped and minimally utilised at present relative to other local macroalgae, farming of the genus might successfully reduce the pressure on existing food production by generating a bioethanol feedstock supply for island nations.

Outside of the Philippines, *Sargassum* spp. have received attention, especially in Japan. Aizawa [13] described a project proposal of mass macroalgae bioethanol production in Japan canvassing the development of extensive farms of *Sargassum horneri*. The proposal modelled the use of 4.47 million km^2 of unused areas of the exclusive economic zone and maritime belts of Japan. Aizawa [13] stated conversion efficiencies from 1 t of raw *S. horneri* (90% moisture, 5.8% carbohydrate) when dried and fermented to approximately 29.6 kg,

or 38 L of bioethanol, based on theoretical conversion for alginate with a productivity rate of 3348 t *Sargassum* km^{-2} ($\sim$9 g m^{-2} day^{-1}) using deepwater floating technology. Using the yield and conversion assumptions of the Aizawa et al. [13] research of 38 L t^{-1} of raw feedstock, in theory the Philippines will need to farm and harvest around 5,761,000 t of *S. horneri* to have achieved the 219 mL annual fuel demand for 2010. Considering that the Philippines farmed 1,666,000 t of macroalgae in 2008, currently expanding at around 150,000 t $year^{-1}$, with large available production areas remaining, it is not an unrealistic option to develop a new non-food bioethanol macroalgal industry on the back of current mariculture capability.

5. Conclusions

Macroalgae represent an unrealised potential to expand existing mariculture industries, and to diversify gasoline supply from mineral fuel imports to domestic bioethanol producers in Pacific island nations. However, industrial-scale marine macroalgae culture requires significant basic research and development for species and cultivar selection, in addition to harvesting and pre-processing technology investment [34]. Furthermore, the development of efficient and cost-effective fermentation processes, and post fermentation markets for macroalgal waste biomass requires further research. The investment stimulus in the Philippines from the Biofuels Act, and the impetus to mitigate both mineral fuel and biofuel imports may provide such an incentive. Nevertheless, the authors recommend a targeted and collaborative range of initiatives focussing on each point in the supply chain from farmer to biorefinery to explore the technical and commercial potential of this new industry.

References

[1] Matsuda S, Kubota H. The feasibility of national fuel-alcohol programs in Southeast Asia. Biomass 1984;4(3):161–82.

[2] Dawe DC, Moya PF, Casiwan CB. Why does the Philippines import rice? Meeting the challenge of trade liberalization. Manila, Philippines: International Rice Research Institute; 2006.

[3] Reyes CM, Sobrevinas AB, Bancolita J, de Jesus J, Philippine Institute for Development Studies Discussion Paper Series (no. 2009–07) Analysis of the impact of changes in the prices of rice and fuel on poverty in the Philippines. Manila, Philippines: Philippine Institute for Development Studies; 2009.

[4] van der Meulen Rodgers Y, Menon N. Impact of the food, fuel, and financial crises on the Philippine labor market; 2010, http://www.people.brandeis.edu/~nmenon/FFF_Crises_Philippines_Draft02.pdf.

[5] Mussatto SI, Dragone G, Guimaraes PMR, Silva JPA, Carneiro LM, Roberto IC, et al. Technological trends, global market, and challenges of bio-ethanol production. Biotechnol Adv 2010;28(6):817–30.

[6] Philippine Department of Energy. Philippine energy plan, 2007–2014. In: Fuelling Philippine development through greater access to energy. Manila, Philippines: Philippine Department of Energy; 2007.

[7] Corpuz PG. Philippine biofuel industry outlook; 2009, http://gain.fas.usda.gov/Recent%20GAIN%20Publications/General%20Report_Manila_Philippines_6-1-2009.pdf.

[8] Poquiz J. Ethanol producers buck biofuels law amendment. Malaya Business Insight; 2010, http://www.malaya.com.ph/07052010/busi4.html.

[9] Gatdula DL. DOE still undecided on ethanol import control. The Philippine Star; 2010, http://www.philstar.com/Article.aspx?articleid=584882.

[10] Galvez M. Seaweed-based biofuel farm to rise in Aurora. The Philippine Star; 2010, http://www.philstar.com/Article.aspx?articleid=573469.

[11] John RP, Anisha GS, Nampoothiri KM, Pandey A. Micro and macroalgal biomass: a renewable source for bioethanol. Bioresour Technol 2011;102:186–93.

[12] Wi SG, Kim HJ, Mahadevan SA, Yang D, Bae H. The potential value of the seaweed Ceylon moss (*Gelidium amansii*) as an alternative bioenergy resource. Bioresour Technol 2009;100:6658–60.

[13] Aizawa M, Asaoka K, Atsumi M, Sakou T. Seaweed bioethanol production in Japan-the Ocean Sunrise Project. Oceans 2007. Vancouver, British Colombia, Canada; 2007.

[14] Goh CS. Lee KT A visionary and conceptual macroalgae-based third generation bioethanol (TGB) biorefinery in Sabah, Malaysia as an underlay for renewable and sustainable development. Renew Sust Energy Rev 2010;14(2):42–848.

[15] Adams J, Gallagher J, Donnison I. Fermentation study on *Saccharina latissima* for bioethanol production considering variable pre-treatments. J Appl Phycol 2009;21:569–74.

[16] Ganzon-Fortes ET. Characteristics and economic importance of seaweeds. In: Proceedings of the seaweed research training and workshop for project leaders. Philippine Council for Aquatic and Marine Research and Development. 1991.

[17] U.S. Department of Energy. National algal biofuels technology roadmap. In: Biomass program. College Park, Maryland: U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy; 2010.

[18] Trono Jr GC, Ganzon-Fortes E. Philippine seaweeds. Philippines: National Bookstore Inc.; 1988.

[19] Percival E, McDowell RH. Chemistry and enzymology of marine algal polysaccharides. London/UK/New York, USA: Academic Press; 1967.

[20] Davis TA, Volesky B, Mucci A. A review of the biochemistry of heavy metal biosorption by brown algae. Water Res 2003;37(18):4311–30.

[21] Horn SJ, Aasen IM, Ostgaard K. Ethanol production from seaweed extract. J Ind Microbiol Biotechnol 2000;25:249–54.

[22] Lewin RA. Physiology and biochemistry of algae. New York, USA and London, UK: Academic Press; 1962.

[23] Rivera HM. Parametric study on pretreatment and saccharification of macroalga (*Sargassum kushimonte*) for hydrolysate preparation. Unpublished BS Chemical Engineering Thesis. University of the Philippines Los Banos, College, Laguna; 2010.

[24] Reyes KMC. Parametric study on pretreatment and saccharification of *Sargassum cristaefolium* for hydrolysate preparation in bioethanol production. Unpublished BS Chemical Engineering Thesis. University of the Philippines Los Banos, College, Laguna; 2010.

[25] Miyanishi N, Inaba Y, Okuma H, Imada C, Watanabe E. Amperometric determination of laminarin using immobilized B-1,3 glucanase. Biosens Bioelectron 2004;19:557–62.

[26] Reed RH, Davison IR, Chudek JA, Foster R. The osmotic role of mannitol in the Phaeophyta: an appraisal. Phycologia 1985;24(1):35–47.

[27] Horn SJ, Aasen IM, Ostgaard K. Production of ethanol from mannitol by *Zymobacter palmae*. J Ind Microbiol Biotechnol 2000;24:51–7.

[28] Borowitzka M. Algal biotechnology products and processes – matching science and economics. J Appl Phycol 1992;4:267–79.

[29] Ge L, Wang P, Mou H. Study on saccharification techniques of seaweed wastes for the transformation of ethanol. Renew Energy 2011;36(84–89), doi:10.1016/j.renene.2010.06.001.

[30] Montaño MNE, Rodriguez MRC, Balitaan RL. Ethnobotany of *Sargassum* spp. in the Philippines. Costal Mar Sci 2006;30(1):222–5.

[31] Trono Jr GC. The genus *Sargassum* in the Philippines. In: Abbot IA, editor. Taxonomy of economic seaweeds with reference to some Pacific and western Atlantic species, California Sea Grant College Program, vol. 3. La Jolla, CA, USA: University of California; 1992. p. 43–94.

[32] Trono Jr GC. The seaweed resources of the Philippines. In: Critchley AT, Ohno M, editors. Seaweed resources of the world. Japan: Japan International Cooperation Agency; 1998.

[33] Montaño MNE. Products and research proposals on *Sargassum* spp. in the Philippines. Seaweed Industry Association of the Philippines; 2009, http://siap.com.ph/wordpress/wp-content/uploads/2009/11/NAST_RTD_on_Sargassum1-Compatibility-Mode.pdf.

[34] Roesijadi G, Copping AE, Huesemann MH, Forster J, Benemann JR. Techno-economic feasibility analysis of offshore seaweed farming for bioenergy and biobased products. In: Independent research and development report IR number: PNWD-3931. Richland. Washington, USA: Battelle and Pacific Northwest Division; 2008.

[35] Horn SJ. Bioenergy from brown seaweeds. Unpublished Doktor Ingeniør Thesis. Norwegian University of Science and Technology, Trondheim, Norway; 2000.